SYNTHETICAL APPLICATIONS OF ACTIVATED METAL CATALYSTS*

XIX. A COMPARISON OF THE EFFICIENCIES OF CATALYSTS DERIVED FROM THE METALS OF GROUP VIII AND FROM COPPER IN THE FORMATION OF BIARYLS FROM PYRIDINE AND QUINOLINE

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The formation of 2,2′-biaryls from pyridine and related bases is known to occur in the presence of a variety of metal catalysts. These include iron-on-asbestos,[1] nickel-on-asbestos,[1] nickel-on-alumina,[2-6] several Raney nickel catalysts,[7-9] and palladium-on-carbon.[10,11] Only catalysts of the last two groups appear to be active at atmospheric pressure, the other catalysts having been used only at elevated pressures.

The present communication records results of a comparison of the activities in the formation of 2,2′-bipyridyl from pyridine of catalysts of all metals of Group VIII and of copper at *c.*115° at atmospheric pressure. The catalysts examined include Raney catalysts of iron, cobalt, nickel, and copper, three supported nickel catalysts, a copper–chromite catalyst, a palladium-on-alumina catalyst, as well as carbon-supported catalysts of ruthenium, rhodium, palladium, osmium, iridium, and platinum. The activities of the carbon-supported catalysts in the formation of 2,2′-biquinolyl from quinoline at *c.*235° at atmospheric pressure have also been investigated.

The results obtained in the present work are summarized in Table 1 which also contains data obtained previously. It may be seen that only catalysts derived from nickel and palladium possess useful activities in the formation of 2,2′-bipyridyl. Among the nickel catalysts only Raney nickel catalysts prepared from nickel–aluminium alloy were effective. A Raney catalyst prepared from nickel–magnesium alloy and a nickel catalyst which had been precipitated with zinc showed very little

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TABLE 1

YIELDS OF BIARYLS OBTAINED FROM CATALYSTS DERIVED FROM THE METALS OF GROUP VIII AND FROM COPPER

Catalyst	Yield of 2,2′-Bipyridyl* (g)	Yield of 2,2′-Biquinolyl* (g)
Raney iron		
Undegassed	0·00016†	
Degassed	0·173	
Raney cobalt		
Degassed	0·0048†	
Raney nickel		
From magnesium alloy, degassed	0·4	
Prepared by addition of NaOH to the alloy,[16] degassed	3·0	
W7–J[8]	4·8[8]	1·36‡,[12] 0·4§[12]
W1[13]	3·15[13]	
Nickel precipitated with zinc, degassed	0·09	
Nickel-on-kieselguhr (10%)‖	—	
Nickel-on-kieselguhr (50%)‖	—	
Nickel-on-silica (62%)‖	—	
Ruthenium-on-carbon	—	
Rhodium-on-carbon‖	—	22¶
Palladium-on-carbon‖	3·94	7·0
Palladium-on-carbon	0·565	3·3
Palladium-on-alumina	Trace	
Osmium-on-carbon	—	—
Iridium-on-carbon	—	—
Platinum-on-carbon‖	—	
Platinum-on-carbon	—	—
Platinum-on-asbestos	—[14]	
Raney copper		
Undegassed	—	
Degassed	—	
Reduced copper	—[14]	
Copper–chromite	—	

* Calculated for 10 g of catalyst.
† Yield determined colorimetrically.[15,16]
‡ At *c.* 110°.
§ At *c.* 235°.
‖ Commercial catalyst.
¶ 2,3′-Biquinolyl (8 g) was also isolated.

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activity, and the supported nickel catalysts were completely inert. These observations show that the presence of aluminium in Raney nickel is essential for the activity of these catalysts in the formation of 2,2′-bipyridyl. This conclusion is consistent with current views about the nature of Raney nickel[17] and with the mechanism previously discussed for this reaction.[9]

The finding that palladium-on-alumina in contrast to palladium-on-carbon possesses very little activity indicates that the support plays an essential part in the reactions with palladium. This fact is reminiscent of the observation that palladium is particularly effective in the dehydrogenation of hydroaromatic compounds when supported on carbon.[18]

The activity of Raney iron in the formation of 2,2′-bipyridyl remains in doubt as the iron–aluminium alloy used in the present work was found to contain *c.* 1·45% of nickel. Raney cobalt has now been found to possess some activity in this reaction. This finding disagrees with earlier experiments with Raney cobalt catalysts in which 2,2′-bipyridyl was not detected.[14] Nickel could not be found in the cobalt–aluminium alloy employed in the present experiments. However, the possibility that traces of nickel caused the activity of the Raney cobalt used in the present work cannot be excluded.

Among the carbon-supported catalysts only palladium and rhodium catalysts were effective in catalysing the formation of 2,2′-biquinolyl from quinoline. The yields of 2,2′-biquinolyl and of 2,2′-bipyridyl obtained with two palladium-on-carbon catalysts differed by *c.* 100%, but the factors responsible for this difference in activity have not been established. In contrast to the findings of Rapoport, and his associates,[10] traces of at least three other bases were detected by paper chromatography. No attempt was made to identify these compounds.

Rhodium-on-carbon has now been found to be the most active metal catalyst in the synthesis of 2,2′-biquinolyl from quinoline. It is of interest that this catalyst causes the formation of appreciable quantities of 2,3′-biquinolyl also. The fact that the same catalyst is inactive in the formation of 2,2′-bipyridyl may be related to the difference in the reaction temperatures. Further work with this catalyst is currently in progress.

Catalysts derived from ruthenium, osmium, iridium, and platinum did not yield detectable quantities of 2,2′-biquinolyl. In these experiments, quinoline was recovered in *c.* 97% yield. However, traces of high-boiling products were detected by paper chromatography. These compounds have not been identified.

Experimental

(*a*) *General.*—The microanalysis was performed by the Australian Microanalytical Service, Melbourne. Ultraviolet spectra were determined with an Optica CF4 recording spectrophotometer. Colorimetric estimations were carried out with a Coleman Universal Spectrophotometer model 14. Analyses involving gas chromatography were carried out with a Griffin VPC apparatus Mk. II equipped with a 6 ft column packed with Celite (40–60 mesh; coated with 15% Apiezon L). The solvent n-butanol–concentrated HCl–water (8 : 2 : 6) was used for the paper chromatography of bases.

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(*b*) *Materials.—Catalysts.* The following alloys were obtained commercially: Iron–aluminium alloy (1 : 1; Fluka A.G.), cobalt aluminium (3 : 7; Light & Co.), nickel–aluminium alloy (1 : 1; B.D.H.), nickel–magnesium alloy (1 : 1; Fluka A.G.), and copper–aluminium alloy (1 : 1; Fluka A.G.). A gravimetric analysis of the cobalt–aluminium alloy failed to show the presence of nickel.[19] The iron–aluminium alloy, however, was found to contain nickel (1·44% gravimetrically;[19] 1·46% by polarographic analysis). Raney iron and Raney copper were prepared according to Johnston, Heikes, and Petrolo.[20] Raney cobalt was prepared by the method given by Billica and Adkins for the preparation of W7 Raney nickel.[21] Raney iron, Raney cobalt, Raney nickel (from nickel–magnesium alloy), and Raney copper were degassed like W7–J Raney nickel.[8] When heated *in vacuo* these catalysts did not undergo any detectable exothermic changes. A Raney nickel catalyst prepared by the addition of NaOH to nickel–aluminium alloy[22], and a nickel catalyst, prepared by precipitation from nickel chloride (138 g in 1 l. of water) with zinc dust,[23] were degassed similarly. Nickel on Kieselguhr (10%) was obtained commercially (Fluka A.G.). Nicat NP/K50 catalyst (50% nickel on Kieselguhr) and Nicat NP/AC60 catalyst (62% nickel on silica) were obtained from Crosfield Chemicals. Copper chromite catalyst was prepared according to Lazier and Arnold.[24] One of the palladium-on-carbon catalysts and one of the platinum catalysts as well as the rhodium-on-carbon catalyst were obtained commercially (Baker). A palladium-on-carbon[25] and a palladium-on-alumina catalyst[26] were prepared from the metal chloride by reduction with formaldehyde in the presence of activated carbon (B.D.H.; washed with nitric acid[25]) or alumina (B.D.H.; for chromatographic adsorption analysis). A platinum-on-carbon catalyst was similarly prepared from hexachloroplatinic acid.[18] Ruthenium-on-carbon and iridium-on-carbon were prepared from the corresponding chlorides as described by Zelinsky and Turowa-Pollak[27] for the corresponding asbestos-supported catalysts. Osmium-on-carbon was prepared from osmium tetroxide by the procedure given by the same authors for the preparation of osmium-on-asbestos.[28]

Unless otherwise stated, all supported catalysts used in the present work contained 5% by weight of the corresponding metal.

Pyridine. Pyridine (B.D.H.; Laboratory Reagent) to which water (5 ml/l) had been added, was fractionally distilled through the column described (reflux ratio 1 : 10).[29] Fractions boiling below 115° were discarded; the fraction b.p. 115–115·5° was redistilled through the same column. Pyridine treated in this way was free of impurities as indicated by paper chromatography or gas chromatography, and it did not give a colour with a solution of *p*-dimethylaminobenzaldehyde in hydrochloric acid.[8]

Quinoline. Synthetical quinoline (B.D.H.) which had been fractionally distilled was satisfactory (gas chromatography and paper chromatography).

(*c*) *Pyridine and Raney Catalysts.*—(i) *Degassed Raney Iron.* Pyridine (50 ml) was refluxed in the presence of the catalyst (from 20 g of alloy) for 50 hr. The reaction was worked up as described to give 2,2′-bipyridyl (0·173 g), m.p. and mixed m.p. 68–70°.[7] This product contained a small quantity of 2,2′,6′,2″-terpyridyl, as shown by paper chromatography.[30]

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(ii) *Raney Iron.* An experiment was carried out as described in (i) above. 2,2′-Bipyridyl was detected by paper chromatography (R_F 0·46; red colour when sprayed with ferrous sulphate); its yield (0·00016 g) was determined by colorimetric estimation of its ferrous chelate compound.[15,16]

(iii) *Degassed Raney Cobalt.* Under the conditions described in (i) above 2,2′-bipyridyl (0·0029 g) was formed. The biaryl was detected by paper chromatography and its yield was determined by colorimetric estimation of its ferrous chelate compound.

(iv) *Raney Copper; Degassed Raney Copper.* Experiments with these catalysts were carried out as described in (i) above. With the techniques described in (ii) above no evidence for the formation of 2,2′-bipyridyl was found.

(v) *Degassed Raney Nickel (prepared from Magnesium Alloy).* Pyridine (100 ml) was refluxed in the presence of the catalyst (from 50 g of alloy) for 50 hr. 2,2′-Bipyridyl (1·06 g) was obtained in the usual way.[7] 2,2′,6′,2″-Terpyridyl was detected by paper chromatography.

(vi) *Degassed Raney Nickel.*[22] Pyridine (150 ml) was refluxed in the presence of the catalyst (from 125 g of alloy) for 50 hr to give 2,2′-bipyridyl (19·0 g) and the nickel(II) complex of 2,2′-bipyridyl and 2,2′-pyrrolylpyridine[31] (0·56 g).

(vii) *Degassed Precipitated Nickel.* Pyridine (150 ml) and catalyst (from 138 g of nickel chloride) were heated at *c.* 115° for 50 hr to give 2,2′-bipyridyl (0·62 g) and the nickel(II) complex of 2,2′-pyrrolylpyridine and 2,2′-bipyridyl (0·03 g).[31]

(*d*) *Pyridine and Miscellaneous Catalysts.*—(i) *Nickel-on-Kieselguhr; Nickel-on-Silica.* Pyridine (32 ml) was refluxed for 24 hr in the presence of each, 10% nickel-on-kieselguhr (2 g; Fluka A.G.), 50% nickel-on-kieselguhr (2 g; Nicat NP/K50), and 62% nickel-on-silica (2 g; Nicat NP/AC60). Evidence for the formation of 2,2′-bipyridyl was not found.

(ii) *Copper Chromite.* 2,2′-Bipyridyl could not be detected after pyridine (16 ml) and catalyst (2 g) had been heated at *c.* 115° for 24 hr.

(iii) *Palladium-on-Alumina.* Under the conditions described in (i)(*e*) following, 2,2′-bipyridyl was formed (less than 0·003 g). The biaryl was identified by paper chromatography.

(*e*) *Pyridine and Carbon-Supported Catalysts.*—(i) *General Procedure.* Pyridine (16 ml) was refluxed in the presence of the catalyst (2 g) for 24 hr. The catalyst was filtered off and washed with hot ethanol (100 ml). Ethanol and pyridine were removed from the filtrate by distillation through a column packed with glass helices. The residue of this distillation was examined by paper chromatography.

(ii) *Palladium.* (1) A commercial catalyst (Baker) yielded 2,2′-bipyridyl (0·788 g), m.p. 70–71°, after one crystallization from light petroleum, b.p. 40–60°. Paper chromatography showed the presence of traces of 2,2′,6′,2″-terpyridyl.

(2) A catalyst prepared from palladium chloride and formaldehyde gave 2,2′-bipyridyl (0·113 g) and traces of 2,2′,6′,2″-terpyridyl (paper chromatography).

(iii) *Ruthenium; Rhodium; Osmium; Iridium; Platinum.* No evidence for the formation of 2,2′-bipyridyl was found.

(*f*) *Experiments with Quinoline and Carbon-Supported Catalysts.*—(i) *General Procedure.* Unless otherwise stated each experiment was carried out by refluxing quinoline (25·8 g) in the presence of the catalyst (2 g) for 24 hr. After the addition of hot chloroform (100 ml) the catalyst was filtered off and washed with hot benzene (100 ml). The solvents were removed by distillation and the reaction product distilled under reduced pressure. The distillates and the residues of the distillation were examined by paper chromatography and gas chromatography.[12]

(ii) *Palladium.* (1) An experiment carried out as described in (i) above gave quinoline (24·8 g), b.p. 120°/21 mm, and a residue (0·85 g). On crystallization from ethanol the latter gave 2,2′-biquinolyl (0·66 g), m.p. 192°, alone and when mixed with an authentic sample. Examination of the liquors of this distillation revealed the presence of at least three other bases.

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(2) Quinoline (10 ml) was heated to reflux over a commercial palladium-on-carbon catalyst (1 g; Baker; 5%). Quinoline (9·0 g) was recovered and 2,2′-biquinolyl (0·70 g) was isolated. Three other bases were detected by paper chromatography.

(iii) *Iridium.* Following the procedure outlined in (i) above, quinoline (25·3 g), b.p. 120°/21 mm and a residue (0·35 g) were obtained. The latter did not react with cuprous ions to give a coloured chelate compound, and 2,2′-biquinolyl could not be detected by paper chromatography.

(iv) *Platinum; Osmium; Ruthenium.* From experiments with each of these catalysts quinoline (25·4 g) was recovered. In each case paper chromatography of the residue of the distillation showed the presence of two compounds neither of which was identical with 2,2′-biquinolyl.

(v) *Rhodium.* Quinoline (64·5 g) was heated for 24 hr at its boiling point in the presence of the catalyst (5 g). After the catalyst had been filtered off it was washed with hot benzene (600 ml) followed by hot ethanol (500 ml). The ethanol washings were collected separately and evaporated to give a brown oil (0·1 g) which was not examined. The benzene washings were freed of solvent and treated with hot ethanol (300 ml) to give 2,2′-biquinolyl (9·0 g), m.p. 190–191°, alone and mixed with an authentic sample. Removal of the ethanol from the mother liquors gave a brown oil (54·9 g) which was treated with ether (200 ml) and 5% HCl (4 × 330 ml). The ethereal layer yielded a brown oil (0·5 g) which was not identified. The basic fraction (54·2 g) was fractionally distilled to give the fractions (1) b.p. 117°/25 mm (5·1 g); and (2) 118°/25 mm (41., 6 g). Quinoline was identified in both fractions by gas and paper chromatography. The latter technique showed the presence of traces of an unidentified base in (2). The residue of the distillation of the basic fraction (7·0 g) was chromatographed on alumina (3 × 20 cm). Elution with petrol (b.p. 60–80°) gave quinoline (0·3 g), characterized as picrate, m.p. 201°, alone and mixed with an authentic sample. Elution was continued with petrol–benzene (1 : 1) to give 2,2′-biquinolyl (1·2 g), followed by colourless plates (1·2 g), m.p. 170–190°. Paper chromatography showed the presence of 2,2′-biquinolyl (R_F 0·65) and 2,3′-biquinolyl (R_F 0·40) in this fraction. Further elution with benzene gave colourless needles of 2,3′-biquinolyl (3·4 g), m.p. 175–176°, lit. m.p. 175–176°[32] (Found: C, 84·5; H, 4·8; N, 10·5%. Calc. for $C_{18}H_{12}N_2$: C, 84·4; H, 4·7; N, 10·9%). The u.v. spectrum of 2,3′-biquinolyl had $\lambda_{max.}$ (log ϵ value) at 257 (4·8) and at 325 mμ (4·2).

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